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Approaches to the design of a novel macromolecular system with tailored optical properties

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Abstract - A systematic approach towards the development of polymeric nonlinear optical material has been presented. The optimally designed functional molecular elements are carefully assembled to incorporate large second and third order optical nonlinearities, paying attention to the processing needs. Preliminary results from the measurement of the optical properties is also presented.

INTRODUCTION

The field of nonlinear optics (NLO) involving organic molecular systems and their macromolecular derivatives is still in its infancy. Nevertheless, it has been a target of intensive research activity in recent years. Given the multidisciplinary nature of this subject, it has attracted the attention of researchers from such diverse disciplines as organic synthesis, material science, optics, and electronics, to name a few. A number of reviews (ref. 1-4) and monographs (ref. 5-7) have recently appeared that provide excellent introduction to this field. There are several reasons for this interest in organic and polymeric materials for NLO. Recent reports have confirmed the anticipated results for a number of molecular crystals that have greatly enhanced NLO properties. Many of these systems have been identified with superior optical characteristics, and faster electro-optic switching times in comparison to their inorganic counterparts. The molecular basis for the NLO properties is beginning to be established. In addition, the relative ease with which various functionalities can be assembled together to arrive at the requisite organic molecular structure provides unique opportunities with this class of materials.

For example, to develop an organic material with a large electro-optic coefficient, it is important that it has a crystalline packing that lacks a center of inversion symmetry (for second order NLO effects). In addition, it should be possible to grow large single crystals that have desirable mechanical and thermal stability and high optical damage threshold. Before undertaking the tedious process of single crystal growth, it is important to assess if a noncentrosymmetric habit is the preferred one, as it usually is not the case. Alternative techniques, however, are available that produce the required acentric molecular organizations, such as electric field induced poling of a guest-host system (ref. 8) (NLO active organic compound, for example, dispersed in a glassy polymer host matrix), Langmuir-Blodgett (L-B) technique (ref. 9), et cetera.

The nonlinear susceptibilities may be further enhanced by cooperativity of the type achieved, for example, in a liquid crystalline (LC) assembly. NLO susceptibilities have been enhanced at least five times because of their spontaneous molecular orientation (ref. 10–12). Polymerization in an ordered system such as in an L-B monolayer or in a liquid crystalline phase may be used to further incorporate extended chain macromolecules with unsaturated electronic structure. These polymer backbones are known to be responsible for large third order susceptibilities. The advantages of polymeric materials in terms of their mechanical strength, processibility, environmental stability, and large damage thresholds cannot be overemphasized. In addition, the ease of synthesis and possibility of chemical modification promise a rich source of new materials for NLO applications.

It is necessary to consider all these discrete aspects in developing a rational approach towards the design, synthesis, and fabrication of NLO active polymeric material systems that can seriously rival the existing inorganic materials such as GaAs, LiNbO₃, et cetera. Indeed, it would further be instructive to explore if these materials would present other new opportunities that are presently not realized. We outline in this paper such an integrated approach to arrive at a class of materials in which the structure has been judiciously optimized to produce highly enhanced second and third order NLO effects. We further anticipate an interesting interplay of these second and third order NLO effects in the same material. These organic and polymeric materials fabricated in the form of thin films as interpenetrating lattices of different electroactive groups are expected to manifest unique properties. An approach to the design and fabrication of novel polymeric superlattices is proposed.

DESIGN AND SYNTHESIS OF NLO ACTIVE ORGANIC COMPOUNDS

Ease of intramolecular charge transfer (ICT) is a criterion of paramount importance (ref. 13) for a large second order electro-optic effect in organic materials. Optimal positioning of strong electron donor and acceptor groups in a conjugate bond system promotes ICT (Fig. 1a). We have chosen azomethine as the conjugate bridging group for the following reasons: (1) the aromatic Schiff base can be produced in high yields by an easy synthetic route; (2) the constituent benzene precursors having the appropriate donor/acceptor substituent groups are commercially available or can be easily synthesized; (3) unlike azo or stilbene derivatives, the azomethines lack a stable cis

stereoisomer and, hence, exhibit little or no photoisomerism; and (4) in addition to the substituents on the benzene rings, the azomethine group itself has electron donor-acceptor character (since it is formed from an aldehyde and an amine), which facilitates ICT. In fact, in accordance with these expectations, a higher value of quadratic NLO susceptibility has been reported recently (ref. 14) for the azomethine derivatives compared to an analogously substituted stilbene derivative.

The molecular structures of a few representative Schiff bases we have synthesized are given in Fig. 1b. The phenol functionality in these compounds, besides promoting ICT, also lends itself for further structural modification into desired derivatives. The representative reactions involved in the synthesis of some useful derivatives are schematically shown in Fig. 2.
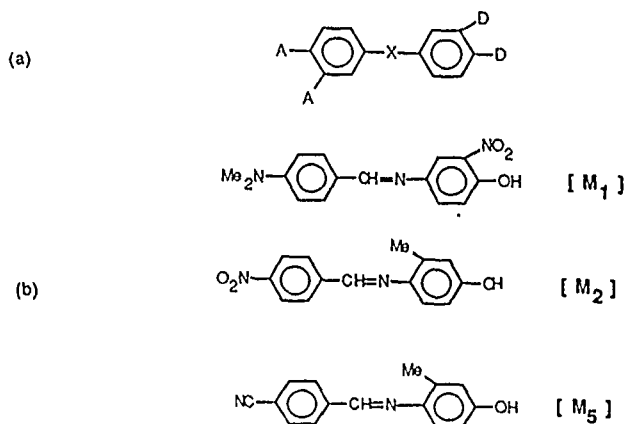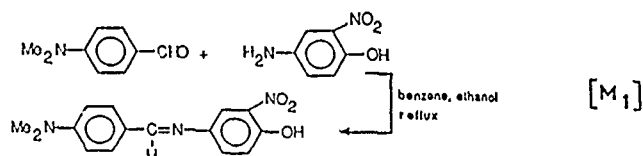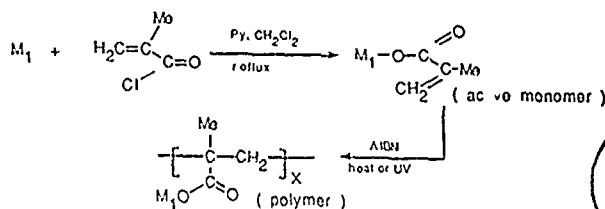

Fig. 1. (a) Design of a NLO active organic compound; A is electron acceptor, D is electron donor, and X is a conjugate bridge such as -C=C-, -N=N-, -CH=N-, etc. (b) Molecular structures of representative Schiff bases.

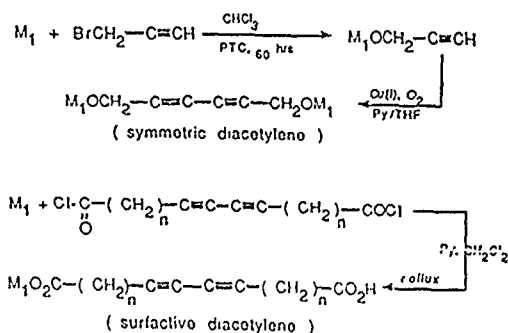Fig. 2. Synthetic scheme showing some representative reactions.

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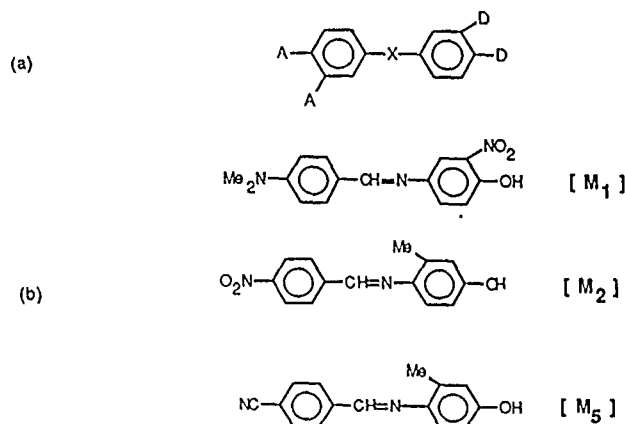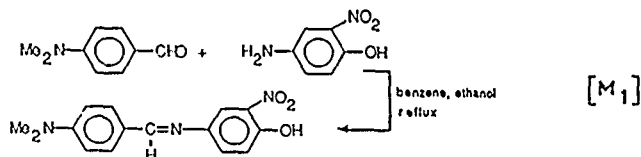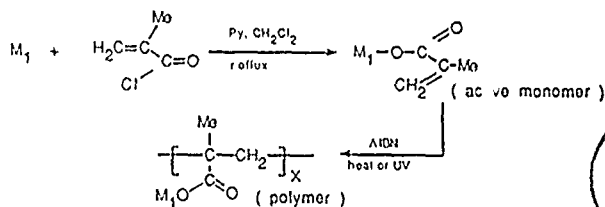

Fig. 1. (a) Design of a NLO active organic compound; A is electron acceptor, D is electron donor, and X is a conjugate bridge such as -C=C-, -N=N-, -CH=N-, etc. (b) Molecular structures of representative Schiff bases.

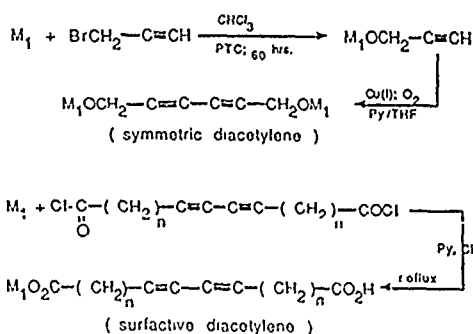Fig. 2. Synthetic scheme showing some representative reactions.

SPECTRAL CHARACTERIZATION AND ESTIMATION OF MOLECULAR HYPERPOLARIZABILITY

The macroscopic crystal susceptibility, $\chi^{(2)}$ for an acentric crystal is proportional to the corresponding molecular nonlinear second order susceptibility, β. In a molecular acentric crystal structure each molecular unit is only weakly coupled to its neighbors (through van der Waals forces) and essentially serves as an independent source of nonlinear susceptibility. Hence an estimation of β can serve as an important index for the assessment of the nonlinear susceptibility of the material in question.

Solvatochromism is a rapid and convenient technique for the determination of molecular hyperpolarizability. This method is based on the experimental observation that the position and the intensity of the absorption band depends on the solvent polarity. This solvent dependent shift in the absorption frequency originates from the same molecular electronic factors (asymmetric charge transfer) as those for β. The relationship can be expressed as (ref. 15):

$$\beta_{xxx} (-2\omega,\omega,\omega) = (3/2\ \hbar^2)\ (\mu_{mn})^2\ (\Delta\mu_{cg})\left\{\omega_n^2\left[(\omega_n^2 - 4\omega^2)\ (\omega_n^2 - \omega^2)\right]\right\} \tag{1}$$

where β_{xxx} is the molecular hyperpolarizability, μ_{mn} is the transition dipole moment, $\Delta\mu_{cg}$ is the difference in the dipole moments between the ground and excited states, ω_n is the charge transfer band frequency, and ω is the excitation beam frequency. μ_{mn} and ω_n can be determined from the uv/vis absorption spectrum.

$\Delta\mu_{cg}$ is determined from the solvatochromic shift in the absorption band in the spectra obtained from solvents of widely varying refractive index, n, and dielectric constant, ϵ. The absorption spectra of a representative material, M_2, for example, exhibiting the solvatochromic shift in cyclohexane and dimethylsulfoxide as solvents is shown in Fig. 3. The estimated β values shown in Table 1 correspond to the data obtained from the absorption spectrum in DMSO. It is important to realize that the calculated value for β is only a rough estimate in view of the error involved in the estimation of the absorption peak intensity or the oscillator strength. Further error is introduced in the estimation of the interaction radius (involved in the estimation of the dipole moment change) (ref. 16) and in the use of the estimated ground state dipole moment for an isolated molecule in the gas phase. Nevertheless, the estimated values of β may be used as an index for comparing the relative merits of a particular molecular structure in promoting second order NLO effects, and suitable structural modifications can be carried out to arrive at the optimized molecular structure through a feed-back of the information from the solvatochromic data.

TABLE 1. Estimated molecular hyperpolarizabilities from solvatochromic data

MATERIAL	λ_{max} cm^{-1}	ϵ_{max} M^{-1}cm^{-1}	μ_g D	μ_{nm} D	$\Delta\omega$ cm^{-1}	$\Delta\mu_{cg}$ D	$\beta_{1.06\mu}$	$\beta_{1.91\mu}$
							(X 10^{30} esu)	
M1	27115	36216	5.68	7.89	1134	13.99	101.0	56.5
M2	24950	12425	2.50	5.32	1415	18.49	88.2	41.5
M5	26652	14082	3.81	5.53	1002	8.80	33.9	18.9

λ_{max} = absorption maximum

ϵ_{max} = molar absorptivity coefficient at λ_{max}

μ_g = ground state dipole moment (estimated by molecular mechanics method)

μ_{nm} = transition dipole moment

$\Delta\mu_{cg}$ = $\mu_c - \mu_g$ = change in dipole moment on excitation

$\Delta\omega$ = solvatochromic shift in frequency

It is seen from Table 1 that these synthesized compounds have their absorption maxima below 450 nm and hence are transparent to both the convenient fundamental laser frequency at 1064 nm obtained from a Nd:YAG Laser and the SHG signal at 532 nm.

SELF ASSEMBLY OF THE ELECTRO-OPTIC MESOGENS

Properties of liquid crystalline (LC) derivatives consisting of NLO active moieties

A large number of mesogenic compounds based on the general structures shown in Fig. 1b were synthesized anticipating spontaneous assembly of the cooperatively interacting electro-optic components. Selected compounds

were further modified to produce polymeric liquid crystals.

The LC compounds discussed here are the intermediate compounds involved in the synthesis of polymeric LC's, whose properties will be discussed elsewhere. The molecular structure and the transition temperatures of the LC compounds are shown in Fig. 4a. The mesomorphic phase in these materials is believed to be nematic as evidenced from the characteristic Schlieren textures observed under a polarized light microscope and from the differential scanning calorimetric measurements.

Fig. 3. Absorption spectra of M_2 in cyclohexane and DMSO displaying solvatochromic shift.

Fig. 4. (a) Molecular structure and transition temperatures of a representative liquid crystalline compound (C = crystal, N = nematic, and I = isotropic); (b) Molecular structure of a representative diacetylene monomer; (c) Schematic diagram showing the experimental set-up for optical modulation/switching using a Kerr cell containing an LC material.

As discussed earlier, the spontaneous molecular orientation characteristic of the LC's tends to enhance the NLO properties in these materials. In view of the intrinsic sensitivity of the LC's to external fields, we can carry out SHG measurements on specimen oriented in an electric or a magnetic field of comparatively low magnitude. The optical field induced birefringence has been observed in LC's where the Kerr constants measured have been shown to be two to three orders of magnitude higher than that for a typical Kerr medium such as nitrobenzene. Results from these NLO experiments with our LC materials will be reported elsewhere.

Optical microscopic investigations indicated that these LC materials display a spontaneous homeotropic (perpendicular to the sample surface) molecular alignment. We have thus obtained LC preparations in which a nearly perfect monodomain homeotropic alignment has been realized. In laser light scattering experiments on

these preparations under different cell geometries interesting LC patterns have been observed that can be correlated with the optical microscopic observations as a function of applied electric field.

The ease with which a monodomain LC organization is obtained makes it attractive to perform an all optical Frederick's transition on these materials. The electric field of the incident optical beam as opposed to the external electric field brings about the orientational changes in this case. This orientation brought about by an intense laser beam can be utilized to demonstrate optical modulation and optical switching (of a weak beam) in these LC materials (Fig. 4c).

Organization of mono- and multilayer assemblies with second and third order NLO properties

A second approach to the assembly of the functional molecules discussed is the use of Langmuir-Blodgett (L-B) technique. Again, the family of molecules with anticipated large β coefficients were suitably modified for L-B growth. Because of the precise control of molecular organization (and hence the sample thickness) NLO measurements can be made on the monolayer and multilayers of these materials. One of the representative materials (shown in Fig. 4a) was used to make a mixed monolayer with stearic acid. The compression isotherm of this mixed monolayer is shown in Fig. 5. A mixed monolayer in 1:2 ratio is used to stabilize the molecule shown in Fig. 4a which is not a classical surfactive molecule. A well-organized monolayer is formed which, however, seems to undergo a number of phase transitions. The optical properties of these films, along with the details of molecular organization, will be reported elsewhere.

These molecules may be further modified to contain a polymerizable entity to not only improve the mechanical stability of the monolayer, but to further enrich the NLO properties. The chemical structure of a diacetylene monomer so derived is represented in Fig. 4b. The molecule contains the diacetylene functionality which undergoes topochemical solid state polymerization from a single crystal monomer to a single crystal polymer. The polydiacetylene so produced has also been shown to possess the highest measured third order NLO susceptibility in the materials' transparent regime. The monomer in our case contains an organic moiety that is expected to exhibit a large second order NLO susceptibility as one of the side groups. The compression isotherm for this and similar monomers have been obtained, and their optical properties will be reported elsewhere. The monolayer or suitably deposited multilayer structures are noncentrosymmetric, and hence second order NLO measurements can be made with these structures. These organized structures can be topochemically polymerized whereby third order NLO properties are enhanced. Thus, multilayered structures using combinations of the structurally rich molecular systems developed so far are expected to possess novel second and third order optical nonlinearities.
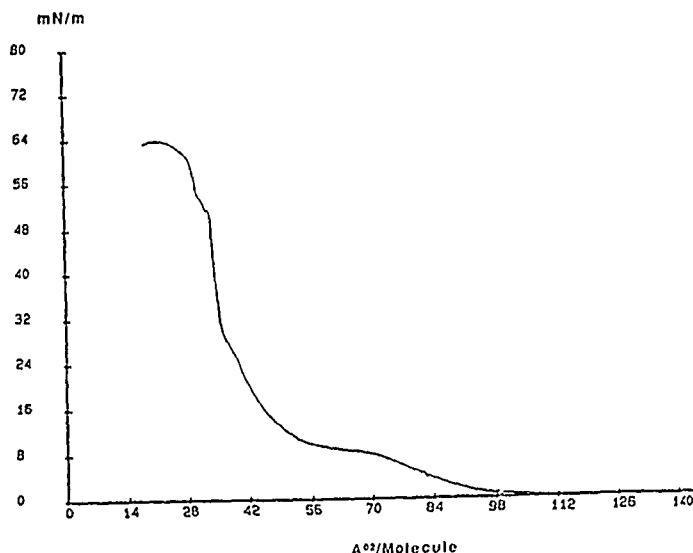

Fig. 5. Compression pressure-area isotherm of the electroactive monomer and stearic acid in the ratio of 1:2.

CONCLUSION

Molecularly engineered materials have been synthesized in which the structural units with optimized NLO characteristics have been judiciously assembled to produce a class of organic superlattices with a unique combination of linear and nonlinear optical properties. Thus, we have integrated molecular structural and electronic property aspects (polarization, ICT, et cetera); liquid crystallinity and the associated control of molecular organization and molecular self-assembly together with the unique electronic properties of the molecular fragments and the polymeric backbone, to elicit a superlative performance from a single synthetic material. The approach to the development of organic superlattices outlined here based on functional, active components is fairly general and may form a framework for the design and development of materials for other novel electronic and optical property aspects.

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POLYDIACETYLENES AND ANALOGIES TO INORGANIC SEMICONDUCTORS AND GRAPHITE

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Abstract

The crystallography and one-dimensional electronic structure of poly-diacetylenes (PDAs) stimulate a variety of chemical and physical studies. ^{13}C CP–MAS n.m.r. studies of the PDAs from PTS and TCDU as well as 1, 1, 4,-4-tetraphenylbutatriene establish the en-yne bond representation for TCDU and rule out a significant contribution from a butatriene form to the ground state at room temperature. The current status of third-order non-linear optical phenomena in PDAs and the conversion of PDAs to conductive materials by ion implantation is presented. Our anisotropic chemical modification of poly-DCH is conceptually distinguished from the usual charge transfer doping of non-crystalline polymers.

Introduction

The polydiacetylenes (PDAs) [1, 2] continue to attract attention as the only class of conjugated carbon polymers available as fully ordered single crystals, a consequence of their preparation by topochemical solid state polymerization. Electron delocalization along the one-dimensional conjugated backbone continues to stimulate inquiries into novel and useful electronic and optical properties of PDAs [3, 4]. Analogies of PDAs to inorganic semiconductors, *e.g.*, Si and GaAs, are invited by quantum chemical calculations [5], which indicate wide bands. The crystallography of PDAs [6], which reveals strong covalent interactions along the conjugated chain and van der Waals forces in the other directions, stimulates analogies to graphite and other layered solids that have covalent forces in a plane, van der Waals forces between planes, and allow intercalation by various reagents.

We describe here recent experimental work stimulated by the analogies cited in the previous paragraph.

En-ynes and butatrienes

Historically, the bond representations of the atoms in the PDA back-bone have been discussed in terms of either the en-yne form (Fig. 1(a)) or
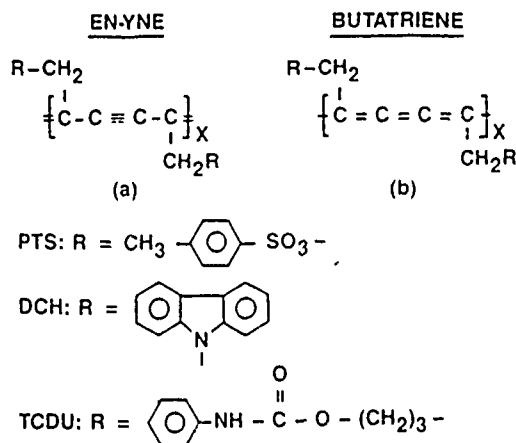
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EN-YNE   BUTATRIENE

R-CH₂   R-CH₂
$$\left\{ \overset{|}{\underset{|}{C}} - C \equiv C - \overset{|}{C} \right\}_X \qquad \left\{ \overset{|}{C} = C = C = \overset{|}{\underset{|}{C}} \right\}_X$$
        CH₂R   CH₂R
        (a)   (b)

PTS: R = CH₃ —⟨O⟩— SO₃⁻

DCH: R = [carbazole structure]

TCDU: R = ⟨O⟩—NH—$\overset{O}{\overset{\|}{C}}$—O—(CH₂)₃—

Fig. 1. Bond representations for PDA backbone structures and molecular structures of R groups.

the butatriene form (Fig. 1(b)). Crystallographic studies [6] of completely polymerized PDAs such as PTS and DCH (Fig. 1) reveal bond lengths supporting the en-yne representation, and quantum chemical calculations [5] of PDA electronic structure indicate that the butatriene representation is significantly higher in energy than the en-yne form. Low-precision crystallographic data [7] have been used to infer a butatriene representation for the PDA TCDU (Fig. 1) [8], a phase that does not polymerize completely [1, 2].
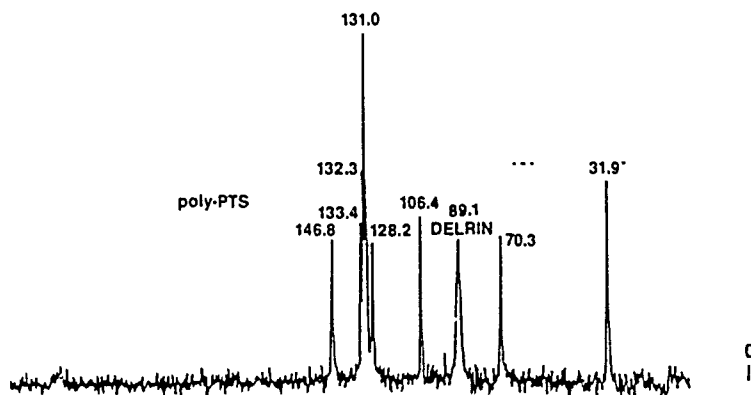

Fig. 2. ¹³C CP–MAS spectrum of poly-PTS. The polyxymethylene (Delrin) resonance is indicated.

In the course of our studies of the linear and non-linear optical properties of PDAs [4, 9], urethane-substituted PDAs such as TCDU became of interest to us because they are melt stable and radiation polymerizable. The relationship between backbone bonding, electronic structure and optical properties prompted us to examine the case of poly-TCDU more closely.

^{13}C cross-polarization magic-angle spinning (CP–MAS) n.m.r. spectroscopy can distinguish between representations (a) and (b) of Fig. 1. Figure 2 displays the ^{13}C CP–MAS spectrum of poly-PTS and confirms the en-yne representation found by X-ray crystallography [6]. In particular, the acetylenic carbon resonance at 106.4 ppm is comparable to acetylene resonances of other PDAs [10 - 12]. The ^{13}C CP–MAS spectrum of poly-TCDU is presented in Fig. 3 with the resonance at 104 ppm assigned to the acetylenic group. Examination of Figs. 2 and 3 reveals the absence of resonances in the range 136 - 171 ppm assignable to a digonal butatriene carbon [13]. The resonance at 146.8 ppm in poly-PTS is that of the aromatic carbon bound to the sulfonate [12].
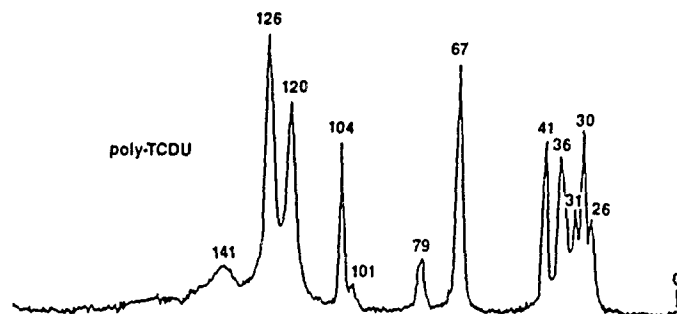
Fig. 3. ^{13}C CP–MAS spectrum of poly-TCDU.

Since there has been no report of a ^{13}C CP–MAS spectrum of an authentic butatriene, we deemed it of interest to do this, and chose the crystallographically defined [14] tetraphenyl derivative. Figure 4 shows the ^{13}C CP–MAS spectrum of this compound; the resonances at 124.1 and 152.9 ppm, comparable to solution data [13], are assigned to the α and β cumulene carbons respectively.
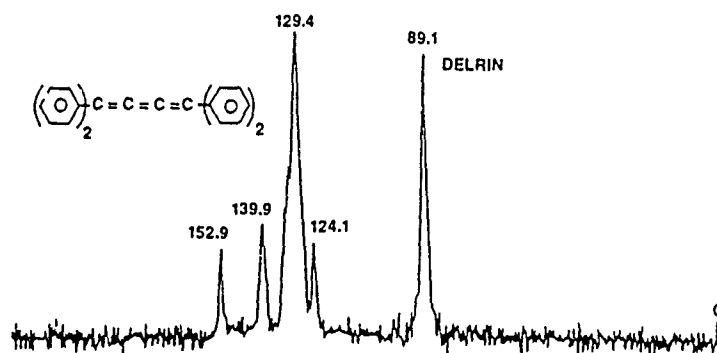

Fig. 4. ^{13}C CP–MAS spectrum of 1, 1, 4, 4-tetraphenylbutatriene. The Delrin resonance is indicated.

We conclude that the existing crystallographic and solid state n.m.r. data for PDAs provide no evidence for a significant contribution from a butatriene structure to the ground state.

Third-order non-linear optical phenomena in solid PDAs

In 1976, Sauteret et al. [15] reported large values of the third-order non-linear optical coefficient ($\chi^{(3)}$), measured along the chain axis in poly-PTS and -TCDU free-standing single crystals in frequency tripling experiments ($\chi^{(3)}(3\omega)$). They inferred that if the non-linearity originated in the intrinsic electronic structure, it may have a subpicosecond response time [15]. Since the values of ($\chi^{(3)}(3\omega)$) reported for PTS [15] were comparable to those of germanium and gallium arsenide, subsequent experimental work has focused on verification of the large values of $\chi^{(3)}$ and measurement of its temporal response.

Research at GTE Laboratories has focused on measurements of the non-linear index of refraction (n_2), which is proportional to the degenerate third-order susceptibility ($\chi^{(3)}(\omega)$), in PDA thin film structures. The latter have been either Langmuir–Blodgett multilayers or thin film single crystals. A comprehensive review of this research has recently been given [9]. Recently, $\chi^{(3)}$ was measured to be 9×10^{-9} e.s.u. at 6515 Å in thin film crystals of poly-PTS, and the material's response time was found to be less than 6 ps [16].

Chemical reactivity of PDAs

Analogies to the partially crystalline $(CH)_x$ and graphite, the observation of low solid state ionization energies in PDAs, and interest in achieving useful electrical conductivity levels have provided the major motivations for the study of reactions of PDAs, and we have summarized the relevant literature [4, 17, 18]. Typically, observed reactions of PDAs have been inhomogeneous and little attention has been devoted to the crystallographic consequences of chemical reactions.

Recently [18 - 20], we have described the anisotropic reactions of electrophilic reagents with poly-DCH. In particular, the reaction of bromine leads to a crystal–crystal transformation in the course of electrophilic bromination of carbazole groups. We have concluded that this process is initially controlled by the energy levels of the carbazole group rather than those of the conjugated backbone [18 - 20].

It is appropriate to contrast our observations on the controlled chemical modification of poly-DCH [18 - 20] with the process of rendering normally insulating polymers conductive by means of charge-transfer reagents, i.e., 'doping'. Doping of a polymer would appear to require at least the following four considerations:

.r.

a

(1) Chemical change occurs.

(2) An electron transfer process is achieved.

(3) As a result of considerations (1) and (2), crystal structure is altered.

(4) The d.c. conductivity of the system is enhanced relative to that of the pristine polymer.

Our chemical modification of poly-DCH with bromine should not be considered a doping because only considerations (1) and (3) above are met. Brominated poly-DCH remains an insulator with d.c. resistivities greater than 10^{10} ohm cm observed in all samples to date. Considerations (1) - (3) are met in the interactions of poly-p-phenylene telluride (PPTe) with oxidants [21] but this polymer is not rendered conductive.

Poly-DCH provides an example of a PDA in which the side chain energy levels control both physical and chemical processes in this solid. In particular, the following situations have been proposed:

(1) Excited state charge transfer from the carbazole singlet state to the conjugated backbone, leading to photocarrier creation [22].

(2) Ground state charge transfer from the backbone to a carbazole cation-radical, leading to dark carrier creation [4, 17].

(3) Anisotropic chemical modification via interaction of electrophilic reagents with the carbazole groups [18 - 20].

Conductive materials by ion implantation of PDAs

Ion beam techniques are of considerable current interest for both preparation and property modification of metals, their alloys, semiconductors, graphite and polymers. We have recently studied the effect of 150 keV [75]As implantation on the PDAs of PTS, DCH and TCDU with respect to modification of the structural, electrical and optical properties of the pristine PDAs [23]. Resonance Raman, X-ray photoelectron and Rutherford backscattering techniques were used to monitor the structural changes. At low and intermediate fluxes of implantation, the ion beam effects changes in the PDA side groups. The electrical properties of poly-DCH change on implantation from an insulator with resistivity of ca. 10^{15} ohm cm at 300 K to a material with a resistivity of 10^{-1} ohm cm when implanted with 5×10^{16} cm^{-2} of [75]As. The temperature dependence of the lowest resistivity materials was studied over the temperature range 20 K $< T$ $<$290 K, and the data were fitted to the equation $\rho(T) = \rho_0 \exp(T_0/T)^m$. At $T > 190$ K, $m \approx 1$ and at $T < 80$ K, $m \approx 0.5$. The former situation is typically associated with thermally activated hopping of carriers between nearest neighbor localized states, while the latter behavior may be associated with variable range hopping in one dimension or the conducting grain model [24]. The observed $\rho(T)$ behavior for implanted poly-DCH may be contrasted [24] with behavior usually observed for implanted non-crystalline polymers, where $m = 0.5$ is observed at all temperatures.

Experimental

Poly-PTS, -DCH and -TCDU were prepared by methods described previously [1, 17], and exhibited X-ray powder patterns which revealed that our samples had the reported crystal structures[6, 7]. Tetraphenylbutatriene was synthesized according to Kuhn and Krauch [25] and had the X-ray powder pattern expected for the reported structure [14]. ^{13}C CP–MAS spectra were recorded as previously described [26].

Conclusions

PDAs provide a novel class of materials in which to study optical, electronic and chemical phenomena that are a consequence of their electronic structure and topography. Indeed, PDAs that can perform both optical and electronic functions are an interesting challenge. While analogies to inorganic semiconductors and layered solids are an interesting framework in which to begin experimentation, further progress will require improved models for electronic structure and spectroscopy as well as continuing interplay between materials design, processing and physical experimentation.

Acknowledgments

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Toward Organic Rectifiers: Langmuir–Blodgett Films and Redox Properties of the N-(4-n-Dodecyloxyphenyl) and N-(1-Pyrenyl) Carbamates of 2-Bromo-5-(2'-hydroxyethoxy)-TCNQ*

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Aviram and co-workers proposed that sandwiches $M_1 | D{-}\sigma{-}A | M_2$ may act as rectifiers of electrical current, where M_1 and M_2 are metallic thin films and $|D{-}\sigma{-}A|$ represents a Langmuir–Blodgett (LB) monolayer of organic molecules $D{-}\sigma{-}A$ with an electron donor (D), an electron acceptor (A) and a covalent bridge (σ). We synthesized DDOP–C–BHTCNQ (1) and Py–C–BHTCNQ (2), the N-(4-n-dodecyloxyphenyl) and the N-(1-pyrenyl) carbamates of 2-bromo-5-(2'-hydroxyethoxy)-TCNQ (BHTCNQ, 3). The cyclic voltammogram (CV) of $D{-}\sigma{-}A$ molecule 1 is almost a superposition of the voltammograms of its D and A ends. The CV of 2 is featureless, because of possible electrocrystallization. Pressure–area (Π–A) isotherms of monolayers of 1 and 2 over H_2O give $\Pi_1 = 38.0$ mN m^{-1}, $A_1 = 0.260$ nm^2 molecule^{-1} at maximum packing for 1 and $\Pi_2 = 28.2$ mN m^{-1}, $A_2 = 0.527$ nm^2 molecule^{-1} for 2. Because of microscopic pinholes, LB films of 1 and 2 did not rectify: low-resistance ohmic behavior was observed for sandwiches Pt | 1 | Hg, Pt | 2 | Hg and SnO_2 | 1 | Hg.

Keywords: Organic rectifiers; Langmuir–Blodgett films; TCNQ Carbamate derivatives

INTRODUCTION

As part of the Organic Rectifier Project[1-4] we report the synthesis, redox properties and Langmuir–Blodgett (LB) film formation[5-8] of DDOP–C–BHTCNQ (1) and Py–C–BHTCNQ (2), the N-(4-n-dodecyloxyphenyl) and N-(1-pyrenyl) carbamates, respectively, of 2-bromo-5-(2'-hydroxyethoxy)-TCNQ[9] (BHTCNQ, 3).‡

$(CHCl_3)$: 3414 cm^{-1} (NH), 2212 and 2218 $(C\equiv N)$, 1729 (C=O), 1590 (δNH). VUV (CH_3CN): 475 nm (log ε 2.89), 410 (3.64), 282 (2.91), 239 (3.39). ^{1}H NMR (CDCl$_3$): δ 7.8–6.5 (6H, ArH and $=C<^H$), 4.8–4.2 (4H, broad singlet, OCH$_2$CH$_2$O), 3.90 (2H, broad triplet, OCH$_2$CH$_2$C$_{10}$H$_{21}$), 2.03–0.63[19H, (CH$_2$)$_{11}$CH$_3$]. ^{13}C NMR (CDCl$_3$): δ155.8, 155.2, 153.1, 149.2, 145.1, 135.6, 130.2, 123.9, 123.6, 120.8, 114.9, 112.3, 107.0 (>C=C< and NCOO), 69.4, 68.4, 61.7 (CH$_2$O), 31.9, 29.6–29.3, 26.0, 22.7, 14.2 [(CH$_2$)$_{11}$CH$_3$]. Analysis: found, C 62.96, H 5.87%; calculated for C$_{33}$H$_{36}$BrN$_5$O$_4$, C 61.30, H 5.62. In the cyclic voltammogram of 1 (Fig. 1) all waves are reversible. The two reduction half-wave potentials, $E_{1/2} = 0.25$ and -0.07 V versus SCE,* are shifted -0.055 and $+0.10$ V from the $E_{1/2} = 0.305$ and -0.170 V measured independently for 3 (measured in 0.1 M Bu$_4$NClO$_4$–CH$_3$CN using a Pt disk electrode;[28] $E_{1/2}$ values for other TCNQ derivatives are given in Refs 29 and 30). The two $E_{1/2}$ values for 1 correspond to the formation of DDOP–C–BHTCNQ$^-$ and DDOP–C–BHTCNQ^{2-}, respectively. The oxidation wave $E_{1/2} = 1.21$ V versus SCE* is shifted slightly from the $E_p = 1.20$ V measured for the methyl ester of 2–N(4–n–dodecyloxy)phenylcarbamic acid (measured in 0.1 M Bu$_4$NClO$_4$–CH$_3$CN using a glassy carbon electrode).[28]
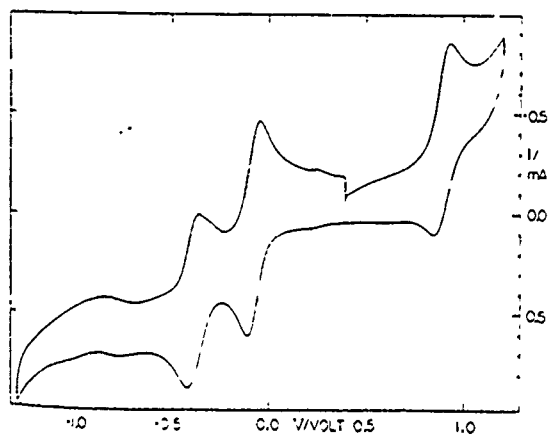
Compound 2 is a red-brown solid, soluble in dimethylformamide and CH$_2$Cl$_2$. It was crystallized from CH$_2$Cl$_2$–hexane. It shrinks at about 180 °C but does not melt below 360 °C. IR (KBr): 3020–2850 cm^{-1} (C–H stretch); 2200 (C≡N); 1705 (C=O), 1520 (amide II); 1200 (C–O stretch); 840 (pyrene). VUV (CH$_2$Cl$_2$): 475 nm (log ε 3.60); 400 (3.62, shoulder); 385 (3.70, shoulder); 343 (4.16); 278 (4.22) and 272 (4.22). ^{1}H NMR (CDCl$_3$): two broad peaks, δ = 8.51 ppm (ca 11H), 4.4 (ca 4H). Analysis: found, C 62.93, H 2.79, N 11.17, Br 13.10%; calculated for C$_{31}$H$_{16}$O$_3$N$_5$Br, C 63.49, H 2.75, N 11.94, Br 13.63. Its visible spectrum shows evidence of association in dimethylformamide (departure from Beer's law); a likely reaction is 2 Py–C–BHTCNQ $\rightleftharpoons$ (Py–C–BHTCNQ)$_2$. The cyclic voltammogram of 2 is almost featureless, possibly because of electrocrystallization.

MONOLAYER FORMATION

Monolayer films for 1 and 2, their pressure-area (Π–A) isotherms (Fig. 2), and LB films were obtained using a Lauda Langmuir trough in a class 100 clean-room. The subphase was Millipore Q deionized water (pH 5.8) of resistivity 1.6×10^7 ohm cm. The compression rate was 0.192 cm^2 s^{-1}.

Compound 1 has three ordering regions (Fig. 2, a1, a2, a3); at the collapse point (a4) $\Pi_1 = 38.0$ mN m^{-1} and $A_1 = 0.260$ nm^2 molecule^{-1} at $T_1 = 292.2$ K. Compound 2 has a single ordering region (b1); at the collapse point (b2) $\Pi_2 = 28.2$ mN m^{-1} and $A_2 = 0.527$ nm^2

Figure 1. Cyclic voltammogram of 1 (0.001 mol l^{-1}) in 0.1 M LiClO$_4$–acetonitrile using Ag–0.1 M AgNO$_3$–0.1 M LiClO$_4$ reference and Pt disk working electrodes.

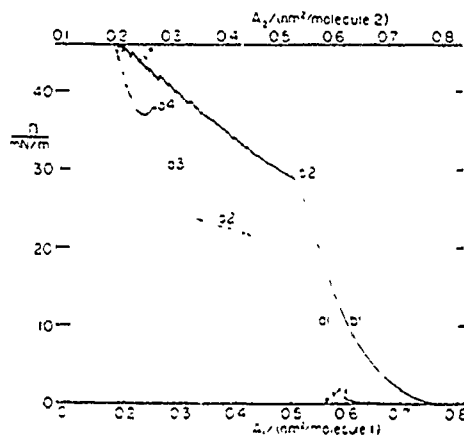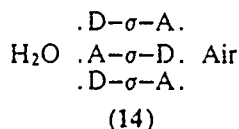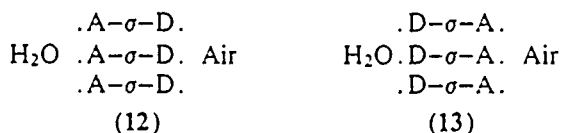*Assuming that V vs (Ag|0.1 M AgNO$_3$ 0.1 M LiClO$_4$) + 0.320 V = V vs SCE.[31]

Figure 2. Pressure–area isotherms for (a) 1 at 292.2 K and (b) 2 at 283.2 K.

molecule^{-1} at $T_2 = 283.2$ K. Alternatively, if one computes the molecular area A' by extrapolating the $\Pi-A$ slope from the collapse points a4, b2 to the $\Pi = 0$ line, then the molecular areas become $A_1' = 0.33$ nm^2 molecule^{-1} for 1 and $A_2' = 0.655$ nm^2 molecule^{-1} for 2.

Assuming that 1 and 2 have flat extended conformations similar to the crystalline conformation of 11,[3,4] their molecular dimensions ($T \times W' \times L$, in nm) are estimated to be $0.39 \times 1.20 \times 3.58$ for 1 and $0.39 \times 1.20 \times 2.19$ for 2. For 2, the calculated area $T_2 \times W_2' = 0.468$ nm^2 is reasonably close to the measured A_2. For 1 the calculated area $T_1 \times W_1' = 0.468$ nm^2 exceeds the measured A_1. If, instead of $T_1 = 0.39$ nm (reasonable for a CH$_2$ group or for Br) we adopt $T_1' = 0.31$ nm (minimum TCNQ–TCNQ stacking distance), then $W_1' = A_1'T_1' = 0.84$ nm is inferred.

Because the dodecyl group in 1 is the more obviously hydrophobic end of the molecule, it seems likely that the films of 1 have the desired geometry 12. For 2, geometries 12 and 13 are both possible, but the undesirable geometry 14 cannot be excluded.

$$\begin{array}{cc} \text{.A–}\sigma\text{–D.} & \text{.D–}\sigma\text{–A.} \\ \text{H}_2\text{O .A–}\sigma\text{–D. Air} \quad & \text{H}_2\text{O .D–}\sigma\text{–A. Air} \\ \text{.A–}\sigma\text{–D.} & \text{.D–}\sigma\text{–A.} \\ (12) & (13) \end{array}$$

$$\begin{array}{c} \text{.D–}\sigma\text{–A.} \\ \text{H}_2\text{O .A–}\sigma\text{–D. Air} \\ \text{.D–}\sigma\text{–A.} \\ (14) \end{array}$$

At present we have no explanation for the molecular organization of 1 in the intermediate ordering region (a1), but it is possible that under moderate pressure some bent conformation of the molecule is stable (e.g. a bend in the carbamate linkage or of the dodecyloxy group relative to the rest of the molecule). Assuming that both 1 and 2 have extended configurations, the measured molecular areas indicate an extremely tight packing for films of 1 and a much looser (or a slanted) packing for compound 2. Since the film thickness was not determined experimentally, these conclusions must remain tentative.

Monolayer LB films of 1 and 2 were picked up (on withdrawal, speed 3 mm min^{-1}) on to microscope slides precoated with a 100 nm layer of evaporated Pt (at $\Pi = 37$ mN m^{-1} for 1 and 28 mN m^{-1} for 2) and on to a conducting SnO$_2$ slide (at $\Pi = 36.7$ mN m^{-1} for 1). The Pt-coated slides were ultrasonically agitated in Micro detergent for 15 min at 50 °C, then rinsed thoroughly with deionized water, ultrasonically agitated in 1:1 HNO$_3$–H$_2$O for 15 min at 50 °C, and rinsed thoroughly before use. The SnO$_2$ slides were ultrasonically agitated in Micro detergent for 15 min at 15 °C, rinsed thoroughly with deionized water, then with reagent-grade chloroform, and dried with pure air before use. Monolayers of 1 and 2 could not be picked up on immersion. For 1, the LB geometry must be glass ¦ Pt ¦ D–σ–A; for 2 the orientation is less certain, for the reasons given above. Multilayer LB film assemblies were not attempted. We could not, in this preliminary study, assess the 'quality' of the monolayer films, i.e. their crystallinity, domain size, etc. However, an effort to demonstrate electrical rectification by monolayers of 1 and 2 was made.

The films are electrically insulating in the plane of the films, but low resistance (1–10 ohm) and ohmic behaviour under both forward and reverse bias was measured through the films (using a 2 mm diameter Hg droplet), perhaps because of microscopic pinholes. It should be noted, however, that under similar conditions it is difficult to obtain high-resistance metal. cadmium arachidate/metal structures when the organic layer is a single monolayer thick. Since such technical problems are often encountered even with such 'well behaved' systems, we therefore argue that a conclusive test of the rectifying properties of LB films of 1 and 2 was not made.

CONCLUSIONS

We have synthesized D–σ–A molecules DDOP–C–BHTCNQ (1) and Py–C–BHTCNQ (2), which form LB films.

The final goal of the Organic Rectifier Project is a rectifier that can be assembled from D–σ–A molecules, where D is a good donor with low ionization potential [TTF (5), N,N,N',N'-tetramethyl-p-phenylenediamine, pyrene, perylene) and A is a good electron acceptor [TCNQ (6)] It should be noted that 1 and 11 have relatively high ionization potentials, and therefore may not be good candidates.

Whereas weak-donor molecules 1 and 11 give good sharp ^{1}H NMR spectra, strong-donor molecules 2, 9 and 10 [and also the recently synthesized[32] N-bis(4-n-dodecylaminophenyl

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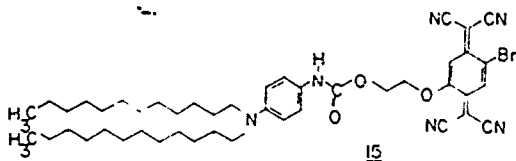
carbamate of BHTCNQ, BDDAP–C–BHTCNQ, 15] give broadened ^{1}H spectra[1-3] for the aromatic rings of the D and A ends of D–σ–A. Whereas the cyclic voltammogram of 1 is, roughly, the expected superposition of the cyclic voltammograms of the isolated D and A ends, this has not been seen for 2, 9, 10 or 15.[32] Some paramagnetism has also been observed in 9, 10 and 15.[32] Intermolecular complex formation or intramolecular conformational equilibria may account for these findings.

The pressure–area isotherms for 1 and 2 show that good, reproducible monolayers of 1 and 2 can be obtained, and the molecular area of 1 indicates a very 'tight' packing mode. Further, these monolayers can be transferred as LB films on to metal substrates. The shorting of the sandwich Pt | 1 | Hg is not surprising, since by the standard lore of LB film work 'bad,' i.e. defect-rich, films are usually obtained on hydrophobic, oxide-free metal surfaces, such as Pt. However, our low-resistance results on SnO_2 | 1 | Hg sandwiches indicate the need for further, careful work.

Acknowledgement

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